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THERMAL STABILITY EVALUATION OF SAMPLES FROM AMMONIUM NITRATE MELT LINE EXPLOSION BY ACCELERATING RATE CALORIMETRY

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THERMAL STABILITY EVALUATION OF SAMPLES FROM AMMONIUM NITRATE MELT LINE EXPLOSION BY ACCELERATING RATE CALORIMETRY

by

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ABSTRACT

An explosion involving a steam-jacketed 99.8% ammonium nitrate line occurred at Western Co-Operative Fertilizers Ltd., Calgary, on September 6, 1984. Ammonium Nitrate samples from the company were tested for thermal stability using an accelerating rate calorimeter. The data demonstrated that the explosion could be caused by overheating inducing decomposition which resulted in a pressure build-up that could not be released in a blocked transfer line. The experiments with conditioned samples also indicated an increase in reactivity of Ammonium Nitrate.

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ÉVALUATION DE LA STABILITÉ THERMIQUE D'ÉCHANTILLONS PROVENANT DE L'EXPLOSION D'UNE CONDUITE DE NITRATE D'AMMONIUM AU MOYEN DE LA CALORIMÉTRIE À RÉGIME ACCÉLÉRÉ

par

P.P. Lee* et R.R. Vandebeek**

RÉSUMÉ

L'explosion d'une conduite constituée à 99,8 % de nitrate d'ammonium et chemisée de vapeur s'est produite à la Western Co-Operative Fertilizers Ltd., à Calgary, le 6 septembre, 1984. Des échantillons de nitrate d'ammonium de la firme en question ont été soumis à des essais afin d'en vérifier la stabilité thermique à l'aide d'un calorimètre à régime accéléré. Les données ont démontré que l'explosion pouvait découler du surchauffage de la décomposition induite qui s'est traduit par une montée de pression qui n'a pu être libérée dans la conduite obstruée. Les expériences qui ont été faites à l'aide d'échantillons conditionnés ont également indiqué une augmentation de la réactivité du nitrate d'ammonium.

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INTRODUCTION

On September 6, 1984, an explosion involving a steam-jacketed 99.8% ammonium nitrate (AN) line took place [1]. The events prior to the explosion, subsequent investigation, and the actions taken to prevent a reoccurrence, are also discussed in the report from the company. The investigation suggested that the most likely explanation of the accident was the heating of the nitrate in a confined space. There was also a suggestion that low levels of metal contamination could catalyse the decomposition reaction. Further studies on samples from the ammonium nitrate melt line using accelerating rate calorimetry were requested.

The accelerating rate calorimeter (ARC) was developed by the Dow Chemical Company and licensed to Columbia Scientific Industries of Austin, Texas. It is an automated laboratory instrument which aides in experimentally determining the time, temperature and pressure relationships of any exothermic reaction in an adiabatic environment. The instrument is used in the industries for the evaluation of thermal hazards. Since the design, operation and performance have been published in the literature [2-4], no discussion of these topics will be repeated.

EXPERIMENTAL

The heat-wait-search operational logic of the ARC was employed in this study. After equilibrium at a start temperature of 150°C, an iterative "5°C heat - 30 min wait - search" sequence was conducted until the appearance of a self-heat rate greater than 0.02°C/min. When an exotherm occurred, time and temperature were monitored continuously until the end of the reaction.

Due to the blockage problem of the pressure measurement line by molten AN, only a wide-mouth cylindrical Hastelloy C bomb, weighing approximately 48 g, was used. Six stainless steel screws secured a rupture disk and a teflon gasket to a flange on the bomb.

In these experiments, part of the heat generated by the exothermic reaction is used in raising the temperature of the bomb and this must be taken into account. The thermal inertia, ϕ, is a critical factor in the analysis where data must be corrected to consider the effect on the response of the system. All the results of testing apply to the sample/bomb system.

Due to the energetic properties of this material, ϕ could only be chosen as close to a real situation ($\phi = 1$) that would result in minimum damage to the calorimeter.

$$\phi = 1 + \frac{C_{v(bomb)} \quad M_{(bomb)}}{C_{v(sample)} \quad M_{(sample)}}$$

where C_v is heat capacity and M is mass.

For most experiments, the weight of sample used was 1.5 g, resulting in a ϕ value of 9. From the information provided by Western Co-operative Fertilizers Ltd., a ϕ value of 1.1 was calculated for the transfer line based on 3" diameter pipe. An experiment was performed using a ϕ value of 2.3 (the lowest attainable value using this system).

The samples (1) (2) and (3) for evaluation were provided by Western Co-operative Fertilizers Ltd., Calgary, Alberta. These were stored at room temperature and ground before testing. The samples were:

(1) solid nitrate plug from detonated pipe
(2) prills with bentonite, but uncoated with stearate
(3) nitrate melt prior to adding bentonite
(4) Sample (3) aged with SS 304 tube in 176°C oven for 17 hours
(5) Sample (3) aged in 176°C oven for 17 hours
(6) AN crystals ACS grade, Anachemia Ltd.

The ARC tests were performed using a Hastelloy C cylindrical bomb, weighing approximately 48 g. The experiments were started at 150°C with a 5°C heat step and a 30 minute wait period.

RESULTS AND DISCUSSION

The AN sample (3) (nitrate melt prior to bentonite addition) from the company came in pieces approximately 2 x 2 x 0.3 cm^3 in size. 18 g of sample (3) was stored in a 170° - 172°C oven to test the visual changes during aging. Smoke evolved after 15 minutes and yellow patches appeared in the sample.

A melting point apparatus by Gallenkamp was used for melting point determination. It was found that sample (3) melted at 163° - 166°C. ACS grade AN crystals was used as control and the melting point was also detected at 163° - 166°C (uncorrected temperature).

A sample bomb was filled fully with 8.9 g AN sample (3) which resulted in a ϕ value of 2.3. This was tested for stability by ARC. The step heat method was used, as described in the experimental section, and the test was stopped manually at a self-heat rate of 0.07°C/min to control the run away reaction and prevent damage. The data provided the following information:

- Phase changes were detected at 85° and 125°C.
- Melting point was in the 164° to 170°C range.
- Temperature rate increased at 180°C with self-heat rate of 0.021°C/min.
- Initial decomposition temperature 187°C.
- Total weight loss after experiment was 1%.
- Exotherm was detected as listed in Table 1.

Table 1. Data on AN sample (3) decomposition, ϕ = 2.3

Time (min)	Temperature (°C)	Self-heat rate (°C/min)
414.36	186.96	0.042
427.80	187.56	0.044
436.31	187.96	0.047
456.88	188.96	0.048
468.71	189.56	0.050
476.33	189.96	0.052
487.51	190.56	0.053
494.48	190.96	0.057
511.83	191.97	0.060
528.03	192.97	0.064
543.28	193.98	0.068
551.92	194.58	0.069
557.39	194.98	0.073

Other tests of thermal stability of AN sample (3) were done using 1.5 g samples, resulting in ϕ values of 9. Accounting for the ϕ effect, the temperature rate increased at 195°C and the exotherm leading to ignition was detected at 217°C. This is comparable to the ACS grade AN crystals. The decomposition data are summarized in Table 2.

Sample (1) (solid nitrate plug from detonated pipe) was tested by step heat method with ϕ value 8.5. The temperature rate started to increase slowly at 190°C. The first slow exotherm occurred at 196°C. The initial temperature of exotherm leading to ignition was detected at 211°C. Also, the ignition was very vigorous rupturing the sealing disks which caused splashing of material and some damage to the calorimeter.

Test result of sample (2) (prills with bentonite, but uncoated with stearate) shows the onset temperature and the decomposition pattern were similar to sample (3), as compared in Table 2 and the figure. The self-heat rate increased slightly at 195°C and the initial temperature was 213°C. No rupture of the sealing disks occurred in duplicate runs of sample (2).

In order to study the effect of thermal aging and metal contaminants on AN decomposition, the ground AN sample (3) was aged with four pieces of SS 304 tube (1/4 inch O.D. x 1/2 inch long) in a 176°C oven for 17 hours. These conditions were designed to simulate the condition of the AN in the transfer line at the time of the explosion incident. The sample was molten with yellow patches. It was cooled, ground into small crystals and stored in a desiccator for ARC testing. As shown in Table 2, the self-heat rate increased slightly at 185°C and the first slow exotherm took place at 191°C. The initial temperature of the exotherm leading to ignition was 213°C and the ignition was very vigorous with rupture of the sealing disk. The occurrence may be caused by thermal aging and metal catalysis of the ammonium nitrate.

Our preliminary work on the reactions of AN and metals (Al, Fe, Pb, Cu, Zn) upon heating indicate that Zn, Cu and Pb react with AN at a temperature below the melting point of AN. The mechanism was not determined.

The effect of thermal aging on AN decomposition was also studied by aging the ground AN sample (3) in a 176°C oven for 17 hours. The sample was melted, cooled, ground and stored in a desiccator for testing. The slight self-heat rate increased at 195°C and the initial temperature of the exotherm leading to ignition was 218°C. This was comparable to that for the untreated AN sample (3). However, vigorous ignition caused rupture of the sealing disk for the duplicate tests.

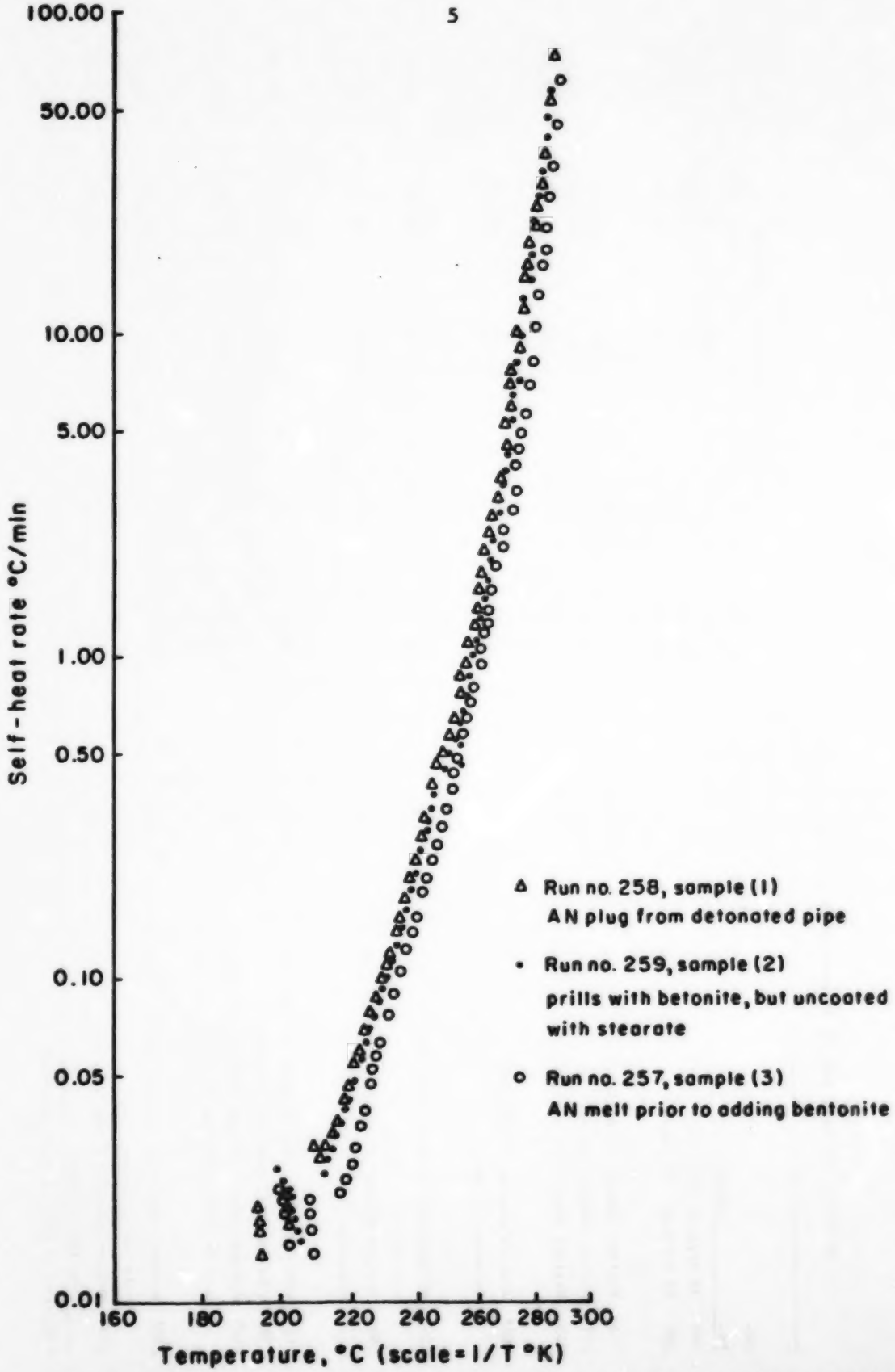

Fig. 1 - Thermal decomposition curves of AN using ARC, step heat method, HC cylindrical bomb, $\phi \sim 9$

Table 2. ARC test data on AN samples by step heat method

Run No.	Sample	ϕ	Decomposition, indicated by + slope increase at (°C)	1st exotherm but stop (°C)	Exotherm leading to ignition			
					Initial temp. (°C)	Initial rate (°C/min)	Temp. (°C) at 0.05°C/min	Temp (°C) at ~ 2°C/min
186	AN crystal, ACS grade	8.7	195	201.22	217.27	0.032	221.07	257.29
206	AN crystal, ACS grade	9.0	195	201.36	215.46	0.022	224.46	262.54
256	Western sample (3) melt AN	2.3	180	-	186.96	0.042	189.56	-
257	Western sample (3) melt AN	8.9	195	201.50	217.09	0.023	227.09	268.20
265	Western sample (3) melt AN	9.1	195	-	216.44	0.021	222.44	250.63
258[a]	Western sample (1) AN from detonated pipe	8.5	190	196.39	211.35	0.030	221.16	264.51
259	Western sample (2) prills with bentonite	9.0	195	201.41	213.41	0.026	223.41	266.52
260	Western sample (2) prills with bentonite	8.7	195	-	213.46 (fluctuate at 206°-213°C)	0.028	222.46	263.51
261	Western sample (3) age with SS 304 tube in 176°C oven for 17 hours	8.7	180	186.29	208.71 (fluctuate at 204°-208°C)	0.023	219.11	262.78
262[a]	Western sample (3) age with SS 304 tube in 176°C oven for 17 hours	9.1	185	191.44	213.44	0.027	220.05	254.50
263[a]	Western sample (3) age in 176°C oven for 17 hours	8.9	195	-	218.07	0.030	226.37	259.26
264[a]	Western sample (3) age in 176°C oven for 17 hours	9.1	195	-	221.56	0.026	225.86	253.74

[a] Rupture of sealing disk occurred

CONCLUSION

The ARC test data indicated that thermally aged samples react more vigorously with higher pressure build-up. The onset decomposition temperatures for sample (1), AN from detonated pipe, and AN aged with SS 304 tube were detected at a lower temperature than the non-aged AN sample. Since the transfer line was blocked, the heating induced decomposition resulted in a pressure build-up that could not be released resulting in an explosion.

A large number of problems can be encountered with an investigation of the thermal hazard potential of a system. The complex mechanisms involved in the exothermic reaction under investigation cannot be described by any single elementary reaction. The limitations imposed by the physical aspect of the instrument such as sensitivity, experimental system, and thermal inertia in the ARC must be considered.

Safety in processing, storage and transportation is normally achieved by means of thermal hazard evaluation. It may specify the normal operating conditions and the action to be taken in the runaway thermochemical reactions. Due to lack of information in correlating the experimental data to the large scale manufacturing process, the data have to be interpreted very carefully. The self-heat rate which is detected at a very slow rate does not necessarily imply a hazard in normal processing. However, the heat generation data as a function of temperature could be used by the engineer to determine the operating temperature and the active cooling system required.

The large scale testing of AN decomposition is planned in the near future and the results will be reported. It may be possible to determine the onset decomposition temperature which correlates the laboratory scale experimental data to large scale operation.

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